

Nonlinear light absorption of polymethine dyes in liquid and solid media

Olga V. Przhonska,* Jin Hong Lim, David J. Hagan, and Eric W. Van Stryland

Center for Research and Education in Optics and Lasers (CREOL), University of Central Florida,
Orlando, Florida 32816-2700

Mikhail V. Bondar

Institute of Physics, National Academy of Sciences of Ukraine, Prospect Nauki 46, Kiev-22, 252650, Ukraine

Yurij L. Slominsky

Institute of Organic Chemistry, National Academy of Sciences of Ukraine,
Murmanskaya 5, Kiev-94, 253660, Ukraine

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We investigate nonlinear optical absorption of a series of polymethine dyes in liquid solution and in a solid poly(urethane acrylate) elastopolymer host. Depending on the ratio between the absorption cross section from the ground to the first excited state (σ_{01}) and from the first to the higher excited states (σ_{12}) and on the pump wavelength, they demonstrate absorption that either increases or decreases with increasing incident energy density. Our interest is directed at studying the optical limiting behavior of the dyes for sensor protection applications, which requires that σ_{12} be greater than σ_{01} . We performed a detailed investigation of the dynamics of these processes, using Z-scan and pump-probe techniques at the single wavelength of 532 nm. We obtained $\sigma_{12}/\sigma_{01} \approx 80$ for one of the dyes, which is significantly higher than any previously reported value of which we are aware. The linear absorption remained significant, a requirement for good optical limiting. However, at high incident energy density for most of the dyes the increasing absorption converted to a bleaching effect with repeated irradiation. This effect was reversed after several seconds in liquid solutions and several minutes in the polymer host, possibly because of replenishment of the dye by diffusion in both media.

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1. INTRODUCTION

We present the results of a study of nonlinear absorption and its dynamics in a series of polymethine dyes either in solution or in polymeric hosts. In particular, we report the results of picosecond excitation-probe experiments in which we observed the dynamics of the induced transmittance changes and Z-scan experiments to determine nonlinear coefficients. Depending on the frequency difference between the linear absorption resonance and the laser wavelength, 532 nm, we observed saturable absorption (SA) or reverse saturable absorption (RSA)¹: SA was observed when the absorption decreased with increasing input, whereas RSA was observed when the absorption increased with increasing input as the result of excited-state absorption (ESA).

One application of RSA is for passive optical limiting devices that protect sensitive optical components from laser-induced damage.²⁻⁶ Passive optical limiting in which RSA was used in various organic and inorganic materials has already been demonstrated. Among organic dyes, the best results were obtained for metallophthalocyanines and metallonaphthalocyanines in liquid solutions^{7,8} as well as in zinc tetra(*p*-methoxyphenyl) tetrabenzporphyrine.⁹ A primary goal of this study was to determine the nonlinear properties of polymethine dyes

of different structures in liquid (ethanol) and solid (polymeric) matrices of poly(urethane acrylate) (PUA) for possible application in optical limiting devices.

Most RSA dyes are well described by a three-level system [Fig. 1(a)] for picosecond excitation; however, for nanosecond excitation intersystem crossing can become important, and a five-level system including two triplet states is usually more appropriate.⁷ The intersystem crossing time for the polymethine dyes is ~ 2 orders of magnitude longer than the fluorescence lifetime, which allows us to neglect the population of the triplet states for both picosecond and nanosecond excitation.¹⁰ In the phthalocyanines this intersystem crossing has been utilized to extend the optical limiting for longer pulses because the triplet states also exhibit strong absorption.

The dependence of the transmittance on irradiance or fluence [Fig. 1(b)] has been described in many papers (e.g., Refs. 7, 8, 11, and 12). The transmittance depends on the relative values of the ground-state and excited-state cross sections, σ_{01} and σ_{12} , respectively, and on the pumping wavelength; SA is possible for $\sigma_{01} > \sigma_{12}$ [Fig. 1(b), curve 1], and RSA is possible for $\sigma_{01} < \sigma_{12}$ (curve 3). If the pumping irradiance is sufficiently high, SA dominates for all cases because of saturation of both absorption processes between ground and excited and between

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vibrational band of a higher-lying S_2 excited state, which rapidly decays to the bottom of that band.

A description of ESA requires a system of at least three levels, i.e., a level S_2 lying above S_1 , as shown in Fig. 1(a).¹ This higher level permits absorption larger than the ground-state absorption if the product of the excited-state cross section times the population of the S_1 state is larger than the same product for the ground state. In terms of a three-level model, the excitation at the absorption band maximum always corresponds to the case $\sigma_{01} > \sigma_{12}$, i.e., absorption saturation. RSA is possible only at the short-wavelength end of the absorption band, when $\sigma_{01} < \sigma_{12}$, and strong singlet-singlet reabsorption is realized. Scanning the excitation wavelength within the absorption band leads to a variation in both σ_{12} and σ_{01} and consequently to changes in the nonlinear transmittance. An investigation of spectral dependencies of the nonlinear absorption of organic dyes is described in Ref. 11.

One of the more promising approaches to limiting applications is the development of solid guest-host systems.^{15–20} Typically the solid host is a transparent polymer such as poly(methyl methacrylate) (PMMA) or an epoxy compound, and the guest is an organic dye showing optical limiting in solution. The major limitations for the practical application of these polymeric systems are the rather low damage threshold of the host medium (approximately 2–3 J/cm²) and photochemical instability of the dyes. PUA has been shown to have a higher damage threshold than PMMA (Ref. 21) because of its viscoelasticity and may allow for spatial diffusion of the dye molecules, which could lead to self-healing of an optically damaged local volume.

2. MATERIALS AND EXPERIMENTS

Our experiments were made with a series of polymethine dyes, PD 1–PD 5, synthesized at the Institute of Organic Chemistry, Kiev, Ukraine. The room-temperature linear absorption spectra and chemical structure of these dyes are shown in Figs. 2 and 3, respectively. The dyes PD 1–PD 3 are distinguished structurally only by the length of the polymethine chromophore (number of CH=CH

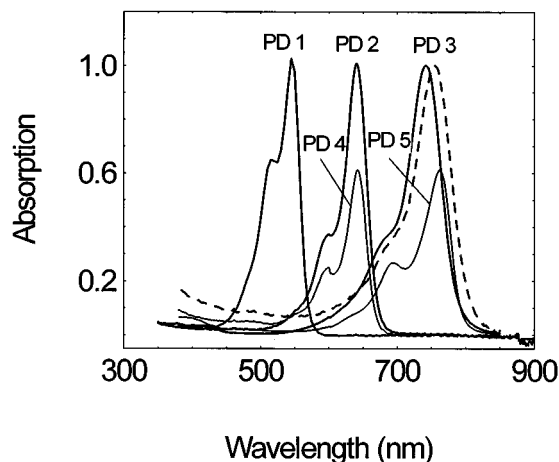


Fig. 3. Normalized absorption spectra of PD 1–PD 5 in ethanol solutions. The dashed curve shows absorption for PD 3 in PUA.

groups, n). Changing n from 1 to 3 leads to a redshift of ≈ 200 nm in the position of the absorption maximum. The main distinguishing feature of PD 4 is the existence of the Cl substitute in the polymethine chromophore. Compared with unsubstituted PD 2, PD 4 has the same position of the absorption maximum but a smaller value of the fluorescence lifetime (τ_F) in ethanol, which may be related to the possibility of rotation of the Cl substitute in the excited state. PD 5 has different end chromophore groups, which change the effective length of the π -conjugated system in the polymethine chromophore. This change leads to a large shift of the absorption maximum to the red region, even for $n = 1$.

The absorption spectra were measured with a Perkin-Elmer 330 spectrophotometer. The concentration of the dyes in absolute ethanol and PUA varies from 10^{-5} to 2×10^{-4} mol/L. This range precludes the formation of dye aggregates. We varied the thickness of the liquid samples from 1 to 5 mm to reach the necessary level of linear transmittance. A typical effect of the polymeric matrix on the absorption band of a polymethine dye is shown in Fig. 3 for PD 3 (the dashed curve is for PUA). The absorption spectrum in PUA demonstrated only a slight shift (≈ 10 nm) toward longer wavelengths without any changes in the structure or the half-width of the main absorption band compared with the ethanol solution. However, during the photopolymerization procedure chemical photoproducts were produced in the sample of PD 3 in PUA that gave rise to a substantial increase in the linear absorption at 532 nm.

Solid polymeric matrices of PUA were obtained by the photopolymerization procedure reported previously.^{10,11} The main feature of PUA compared with organic glasses (for example, PMMA) is the existence at room temperature of a highly elastic state (the glass-transition temperature is ≈ 210 K) characterized by high mobility of the polymeric chain segments compared with the glassy state. This property is responsible for the high resistance of PUA to radiation damage and for its self-healing ability.²¹ Hence this polymeric material can be used under intense pumping irradiation with minimal damage.

The polymeric samples used in this study represent triplexes in which a dye-doped polymeric film (thickness 0.1–2 mm) is placed between two glass plates with strong adhesion between their surfaces and the polymer layer. The plates are necessary for the photopolymerization reaction because atmospheric oxygen inhibits the reaction. These plates also ensure high-optical-quality surfaces and protect the polymeric medium from mechanical damage and long-term atmospheric influences.

We used two well-developed nonlinear characterization techniques, Z scan and pump-probe.^{22–24} The measurements were performed with the second harmonic of a mode-locked Nd:YAG laser (532 nm) that produced single pulses of 30-ps (FWHM) duration and with a repetition rate that varied from 0.5 to 10 Hz.

The Z-scan technique involves measuring the energy transmittance as a function of the sample position Z relative to the focal position of a Gaussian beam. For all Z scans the beam was focused to a waist of radius $21 \mu\text{m}$, half-width at the $1/e^2$ maximum in irradiance ($\text{HW}1/e^2\text{M}$). The range of input energies was

10^{-2} – $10\ \mu\text{J}$. In our experiments we performed open-aperture Z scans, taking care to collect all the transmitted energy, so our measurements were sensitive only to nonlinear absorption.²³

We used pump–probe experiments to determine the dynamics of the nonlinear absorption. These measurements included pumping of the sample by a strong beam, which induced the nonlinearity, and probing the relaxation of this nonlinear response with a delay of as much as 15 ns with a weak beam. The pump beam was focused to a waist of radius $230\ \mu\text{m}$ ($\text{HW1}/e^2\text{M}$) and the probe was focused to a waist of radius $34\ \mu\text{m}$ ($\text{HW1}/e^2\text{M}$) while the probe irradiance was kept much less than that of the pump. The range of pump energies was 10 to $150\ \mu\text{J}$. The angle between the pump and the probe beams was $\approx 5^\circ$.

3. RESULTS

A. Z-Scan Measurements

We studied the nonlinear transmittance of PD 1–PD 5 in ethanol solutions and PUA matrices over a wide range of peak on-axis pumping irradiance from 0.01 to $30\ \text{GW}/\text{cm}^2$ (fluence range 4.5×10^{-4} to $1\ \text{J}/\text{cm}^2$). Irradiance greater than $35\ \text{GW}/\text{cm}^2$ led to damage of the glass cell surfaces and the glass covers of the polymeric samples. The main results are presented in Figs. 4–6. In Fig. 4 we show the open-aperture Z scans for PD 1 and PD 2. For PD 1, in which the 532-nm radiation is near the linear absorption maximum, the response corresponds to SA. However, for PD 2, which differs from PD 1 only in the additional $\text{CH}=\text{CH}$ groups, RSA is observed. This is a clear illustration of how a simple change in resonance can drastically alter the limiting behavior. PD 1 in PUA also shows strong SA, whereas PD 2 in PUA exhibits RSA.

All the samples PD 2–PD 5 exhibit RSA both in ethanol solution and in PUA. This result could be anticipated, as the 532-nm radiation produced excitation into the short-wavelength tail of the absorption band for all these materials. In Fig. 5(a) we show the results obtained for PD 3 in ethanol, which exhibits a ratio of $\sigma_{12}/\sigma_{01} \approx 80$, a figure much larger than previously reported to our knowledge for any organic material in a region where the linear absorption is substantial, $\sigma_{01} = 7 \times 10^{-18}\ \text{cm}^2$. The calculated cross-section ratio σ_{12}/σ_{01} for PD 3 in PUA, however, is much lower. One reason for this large difference is a more than 10-times increase in the linear absorption value, which is reflected in our calculated σ_{01} . This absorption at the pumping wavelength is related to the absorption of the photoproduct of PD 3 obtained in the photopolymerization reaction during the preparation of the sample. Thus the real absorption of the molecules of PD 3 at 532 nm is much less. This observation should be taken into account for improving the technology of preparation of the polymeric samples. Other molecules did not show so large a difference in cross sections between ethanol and PUA hosts, perhaps because of better photostability of these dyes. The cross sections determined from linear and nonlinear absorption measurements for all the dyes in both ethanol and PUA are summarized in Table 1.

For PD 2, PD 3, and PD 4 at high fluence–irradiance the RSA transforms into SA (bleaching) with repeated ir-

radiation. This effect is illustrated for PD 3 in Fig. 5(b) and for PD 4 in Fig. 6. There are two possible explanations for this effect: saturation owing to a fast reabsorption process from S_1 to S_2 (with saturation of the ESA), which was previously reported [Fig. 1(b)],^{8,25,26,27} or photoinduced transformation of the polymethine molecules into some new configuration or species that is non-absorbent at 532 nm.

To distinguish between these two effects we performed Z scans at various repetition rates. We changed the time delay between pulses from 0.1 to 2 s. In addition, we performed Z scans for which the sample was moved to irradiate a fresh site after each pulse. For dyes in liquid solution, increasing the time between pulses led to a decrease of the bleaching effect. Thus there must be a formation and accumulation of a new long-lived state that recovers on a time scale similar to the time between pulses. Our assumption is that the formation of this new state is due to a laser-induced reaction in the excited state of the dye molecule with the appearance of a new product, i.e., a form of photobleaching. This new state could be a state of the same molecule or a new chemical species; we cannot tell the difference in these experiments.

Recovery of photobleaching was also observed in the PUA samples but on much longer time scales than could be realistically measured by changing the laser repetition rate. For this reason we studied these effects with the pump–probe apparatus described below.

Figure 6 illustrates the buildup of the long-lived state for PD 4 in ethanol and in PUA. Z-scan curves for dyedoped PUA are much more asymmetric and show bleaching to a value higher than the original level of linear transmittance. The asymmetry in these curves results from the repeated irradiation and buildup of this product state. All Z scans were scanned from left to right in the figures, so the cumulative effect is larger toward the right. The enhanced cumulative effect (bleaching) observed in the PUA is a combination of the higher level of linear transmittance for the PUA samples and the reduced mobility of the dye molecules.

For sample PD 5 no bleaching of the nonlinear transmittance was observed over a wide range of irradiance (up to $30\ \text{GW}/\text{cm}^2$). This dye is characterized by the smallest value of τ_F among the samples in both ethanol and PUA. Therefore the onset of the nonlinear response occurs at a higher pumping irradiance ($\approx 1\ \text{GW}/\text{cm}^2$), and, in turn, saturation does not begin until $\approx 10\ \text{GW}/\text{cm}^2$.

Up to a pumping irradiance of $30\ \text{GW}/\text{cm}^2$ no damage of the PUA matrix was observed. The damage morphology in PUA is quite different from that in PMMA. Because of the viscoelasticity the main changes in the PUA matrix represent a local volume with a changed refractive index. This index change does not significantly alter the transparency of the matrix.

B. Pump–Probe Measurements

We used pump–probe experiments to determine the dynamics of the nonlinear absorption and the kinetics of the formation and relaxation of the long-lived product state. Figure 7 shows typical experimental results of pump–probe measurements (for PD 2) at low fluence–irradiance,

0.015 J/cm² or 0.5 GW/cm², below inputs required for photoinduced changes in the polymethine dyes. As can be seen, the transmittance of the probe beam decreases on irradiation by the pump pulse (i.e., follows the cumulative pump energy to create excited states). The kinetics of the repopulation of the ground state (recovery of the initial transmittance) are different in ethanol and PUA,

showing the longer excited-state decay time in the polymeric medium. By fitting the curves with rate equations describing the time dependence of the nonlinear transmittance for a three-level model, we determined the decay times. The decay kinetics for PD 2 are almost monoexponential for both ethanol and PUA samples, with decay times of 0.8 ns in ethanol and 5 ns in PUA. The value for

Table 1. Parameters of Polymethine Dyes in Ethanol and PUA

Parameter	Dye									
	PD 1		PD 2		PD 3		PD 4		PD 5	
	Ethanol	PUA	Ethanol	PUA	Ethanol	PUA	Ethanol	PUA	Ethanol	PUA
T_L	0.48	0.65	0.59	0.67	0.64	0.96	0.68	0.91	0.84	0.62
σ_{01} ($\times 10^{17}$ cm ²)	4	29	3	7.4	0.7	12	3.2	4.6	0.7	1.6
σ_{12} ($\times 10^{17}$ cm ²)	1.2 ± 0.2	8 ± 2	15 ± 2	31 ± 2	60 ± 5	26 ± 7	24 ± 3	11 ± 6	5.5 ± 0.6	2.6 ± 0.3
σ_{12}/σ_{01}	0.3 ± 0.1	0.3 ± 0.1	5.2 ± 0.5	4.2 ± 0.3	81 ± 7	2.2 ± 0.6	7.5 ± 1	3.0 ± 1.0	7.9 ± 0.8	1.6 ± 0.2
τ_F (ns)	0.2	2.7	0.8	2.2	0.3	2.1	0.3	2.3	0.03	0.6

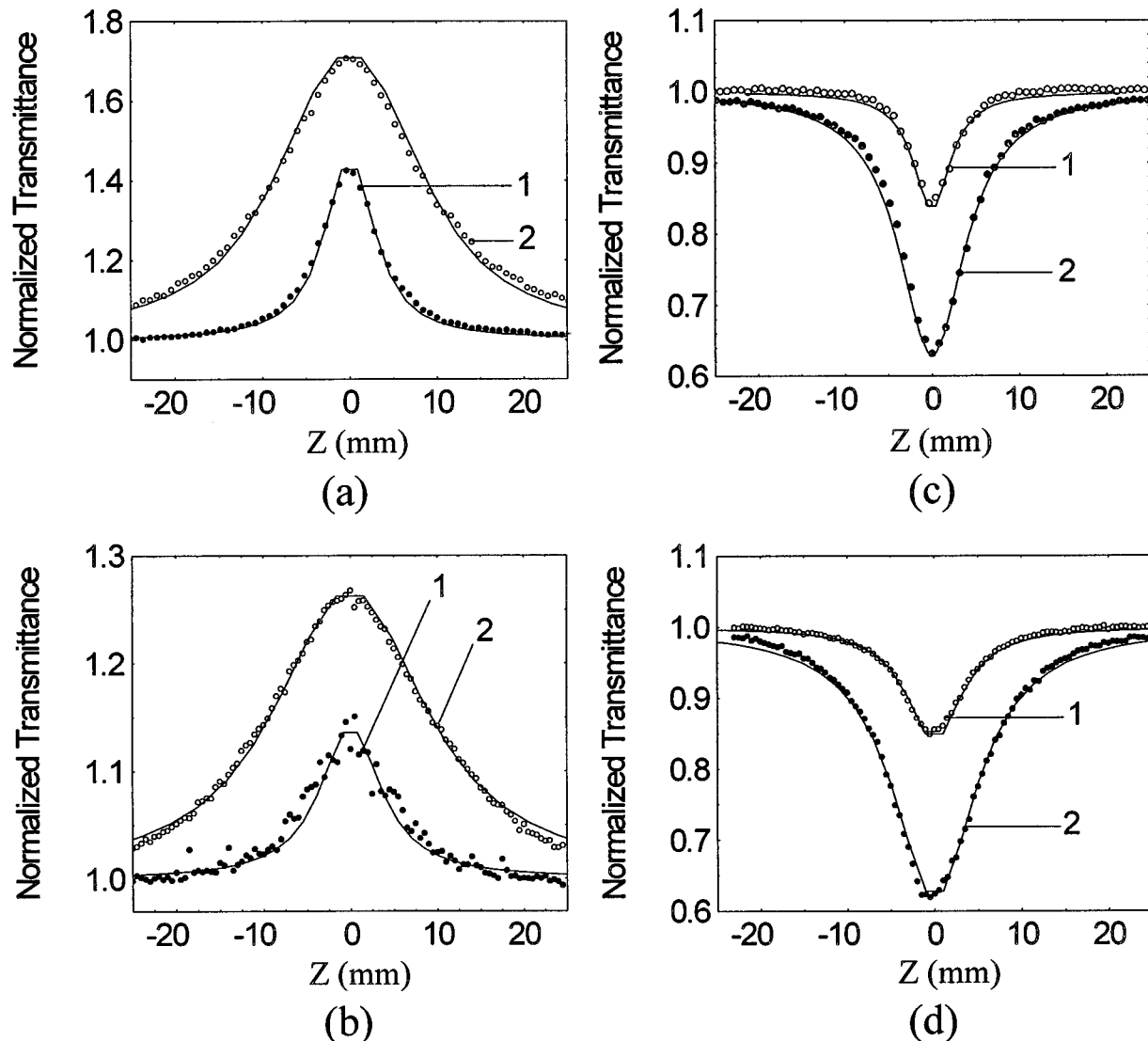


Fig. 4. Z-scan data for PD 1 in (a) ethanol and in (b) PUA matrix and for PD 2 in (c) ethanol and in (d) PUA matrix. (a) Energy $E = 0.1$ (curve 1), $0.5 \mu\text{J}$ (curve 2); (b) $E = 0.03$ (1), $0.3 \mu\text{J}$ (2); (c) $E = 0.1$ (1), $0.5 \mu\text{J}$ (2); (d) $E = 0.1$ (1), $0.5 \mu\text{J}$ (2). The solid curves are numerical fits as described in Section 4.

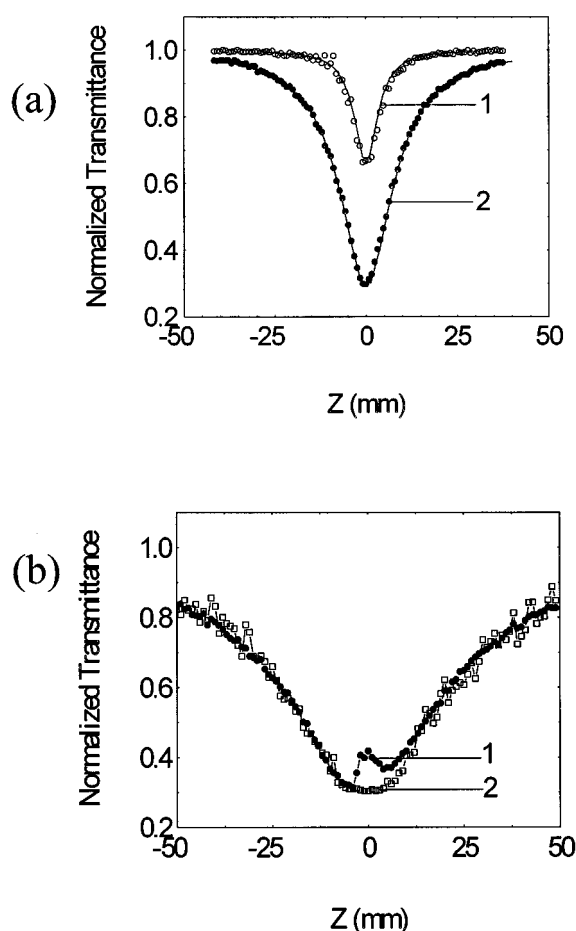


Fig. 5. (a) Z-scan data for PD 3 in ethanol; energy $E = 0.05$ (curve 1), $1.0 \mu\text{J}$ (curve 2). The solid curves are numerical fits as described in Section 4. (b) Z scan at $E = 4.0 \mu\text{J}$ for PD 3 in ethanol for two repetition rates to 10 Hz (curve 1) and 0.5 Hz (curve 2).

the decay time in ethanol is in good agreement with the fluorescence lifetime τ_F of these dye molecules in the first excited state; see Table 1. The value of the decay time in PUA is ~ 2 times greater than τ_F , which possibly reflects the role of the polymeric medium on excited-state relaxation processes of the dye molecules.²⁸ Data on lifetimes for all the dyes are summarized in Table 1.

We also studied the kinetics of the formation and relaxation of the long-lived state by performing repetitive irradiation at fixed temporal delays. Whereas in ethanol solution there was a single relatively rapid recovery of the nonlinearity after repeated irradiation, in PUA we observed two components in the restoration, a relatively fast one (of the order of minutes) and a slow one (of the order of hours or even days). At high inputs this restoration can be incomplete.

4. DISCUSSION

At input fluence (irradiance) levels from 4.5×10^{-4} to 0.36 J/cm^2 (0.01 to 8 GW/cm^2), a three-level model works well in describing the nonlinear behavior of the molecules. Cross sections σ_{12} and σ_{01} determine the optical limiting properties and can be determined from our ex-

periments at low repetition rates and low energies.² First, we calculate the values σ_{01} given by

$$\sigma_{01} = -\frac{\ln(T_L)}{NL}, \quad (1)$$

where T_L is the linear transmittance of the sample at 532 nm determined at low input with the sample positioned far from focus, N is the density of molecules, and L is the thickness of the medium. As described in Ref. 6, given a three-band system, the variation of fluence, F , along the propagation distance, z , can be shown to be given by

$$\frac{dF}{dz} = N \frac{\hbar\omega}{\sigma_{01}} (\sigma_{01} - \sigma_{12}) [\exp(-F\sigma_{01}/\hbar\omega) - 1] - \sigma_{12}NF, \quad (2)$$

where it is assumed that the input pulse width is much less than the excited-state decay times. At low fluence, where saturation can be neglected, the exponential can be expanded to give

$$\frac{dF}{dz} = -NF\sigma_{01} \left[1 + (\sigma_{12} - \sigma_{01}) \frac{F}{2\hbar\omega} \right]. \quad (3)$$

Equation (3), which is directly analogous to that which describes two-photon absorption,²⁹ can be solved for a sample of thickness L as

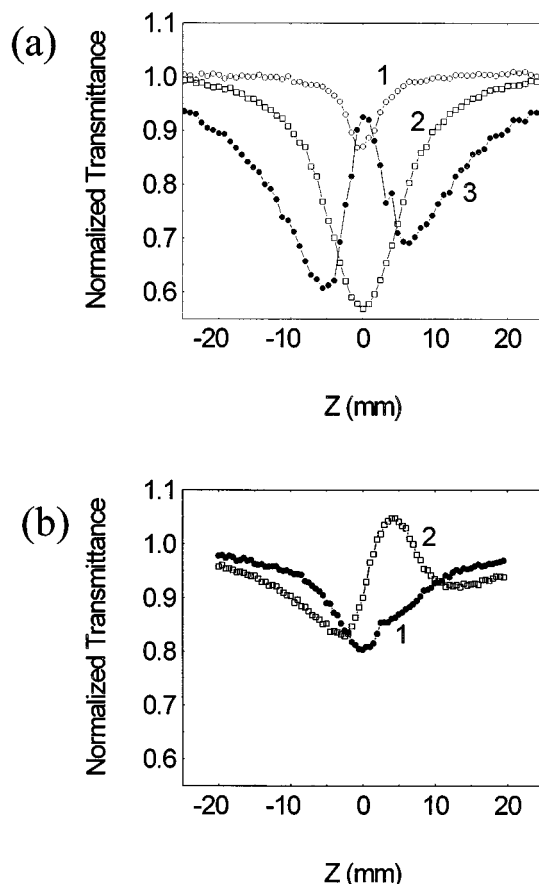


Fig. 6. Z-scan data for PD 4 in (a) ethanol solution and in (b) PUA matrix. (a) $E = 0.05$ (curve 1), 0.5 (curve 2), $2.0 \mu\text{J}$ (curve 3); (b) $E = 0.5$ (curve 1), $2.0 \mu\text{J}$ (curve 2).

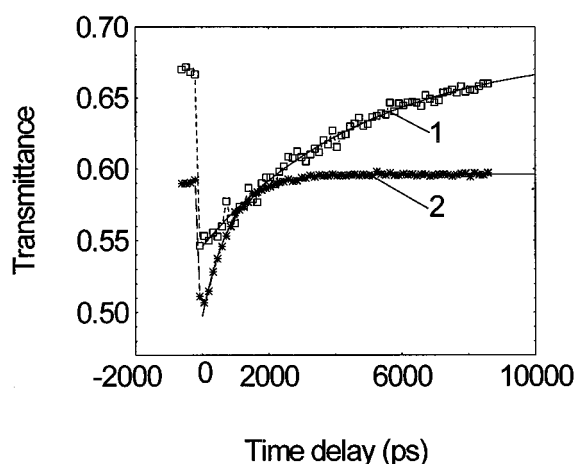


Fig. 7. Results of pump-probe experiments for PD 2 in 1, PUA and 2, ethanol solution at a pumping fluence $F = 0.015 \text{ J/cm}^2$. The solid curves are single exponential fits.

$$F(L) = \frac{F(0)\exp(-\alpha L)}{1 + (\sigma_{12} - \sigma_{01})F(0)[1 - \exp(-\alpha L)]/(2\hbar\omega)}, \quad (4)$$

where the linear absorption coefficient, as measured in an experiment, is $\alpha = N\sigma_{01}$. Thus the parameter fit in a Z-scan experiment is the difference between excited and ground-state cross sections. The normalized energy transmittance, as measured in a Z-scan experiment, is then given by

$$T = \frac{\int_{-\infty}^{\infty} F(L, t) dt}{\int_{-\infty}^{\infty} F(0, t) dt}. \quad (5)$$

The transmittance is a function of sample position Z (as opposed to z , the depth in the sample). In practice we perform the integrals before making the above approximations, but the approximations nicely show how the Z-scan analysis is insensitive to explicit knowledge of the ground-state absorption cross section if $\sigma_{12} \gg \sigma_{01}$. Examples of numerical fits are shown in Figs. 4 and 5(a).

5. CONCLUSION

We have characterized the nonlinear optical properties of several polymethine dyes at 532 nm in two host media, ethanol and the elastopolymeric medium poly(urethane acrylate) (PUA). We found that the type of nonlinear absorption depended on the relative position of the absorption maximum with respect to 532 nm, changing from saturable absorption (SA) near resonance to reverse saturable absorption (RSA) below resonance. We determined the ratio of the excited-state absorption cross section to the ground-state absorption cross section in these materials and found it to be nearly the same in ethanol and in PUA, except for PD 3. PD 3 in ethanol showed by far the largest ratio, $\sigma_{12}/\sigma_{01} = 80$, in ethanol solution; however, this ratio drops in PUA because of an increase in the apparent value of σ_{01} , which is related to the appearance of photoproduct absorption at 532 nm. This in turn leads to

an underestimation of σ_{12} . We conclude that this dye and its derivatives should be investigated further for optical limiting applications.

We also determined the dynamics of the excited-state absorption by performing pump-probe experiments. We found that the excited states decayed in less than a nanosecond in ethanol but of the order of a few nanoseconds in PUA. In both cases this time is less than the time for intersystem crossing to long-lived triplet states. From the point of view of having a good optical limiting material, this result is unfortunate because the accumulation of excited states over the entire pulse width in time gives larger losses. However, the excited-state lifetimes are significantly increased in PUA. Whether intersystem crossing to highly absorbing triplet states is possible in these polymethine dyes remains to be seen.

The dyes PD 1–PD 4 (Table 1) have the same chromophore structure at the end of the polymethine chain and exhibit large nonlinear response. They also show strong saturation effects in the Z-scan data. In particular, the Z-scan traces rapidly broaden in Z for increasing input, indicating that ground-state depletion is significant. These broadening effects are intensified in the polymeric medium because of the increased excited-state lifetime.

At very high inputs ($>8 \text{ GW/cm}^2$ or $>0.36 \text{ J/cm}^2$) a decrease in the level of nonlinear response was observed that appears to be connected to a photochemical reaction of the excited state of the dye molecule, leading to the formation and accumulation of a new product. We suggest that the observed decrease in nonlinear absorption in PD 1–PD 4 may be caused by a photochemical reaction occurring in the excited state, in which a new product is formed that absorbs at shorter wavelengths owing to a decrease in the length of the polymethine chromophore. This process may be irreversible, in which case the observed recovery is controlled by diffusion of fresh molecules into the focal volume, or it may have an extremely slow recovery time. For our experimental conditions the populations of the ground states of these dyes in ethanol solution are restored over a period of several seconds. In the polymeric medium this time is much longer. A more detailed understanding of the mechanism of this process requires additional investigation.

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*Institute of Physics, National Academy of Sciences of Ukraine, Prospect Nauki 46, Kiev-22, 252650, Ukraine.

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